F82

United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/S3-80-093 June 1981

EPA

Project Summary

Application of Fourier Transform Spectroscopy to Air Pollution Problems

NEWARK PUBLIC LIBRARY

AUG 10 1981

U. S. GOVT. PUBS.
DEPOSITORY 376

John W. Spence

In this study, in which Fourier Transform Spectroscopy has been applied to air pollution problems, there are two phases. In the first phase, the results of investigations of the nature of the information that can be retrieved from spectra obtained with Fourier Transform Spectroscopy are presented. It is shown that nonlinear, least-squares analysis of the spectra is capable of retrieving types of information beyond the reach of conventional methods and with improved precision and accuracy. In the second phase of this work, Fourier Transform Infrared Spectroscopy has been employed to study quantitatively the kinetics and reaction mechanisms of several chemical species: peroxynitric acid, hypochlorous acid, and dimethylnitrosamine. Rate constants related to the formation and decay of these species and infrared extinction data necessary for the quantitative analyses of these compounds are determined.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Infrared spectroscopy is used routinely in many laboratories to aid in the identification of the composition of samples and to estimate, quantitatively, the amounts of the individual components of the sample. During the past 30 years there have been continual improvements in the design of infrared spectrometers, and these have led to increased versatility in manipulating the spectra produced. Fourier Transform Spectrometers (FTS) are a new class of spectrometers, and their use has been widespread in the past decade. They allow extended spectral regions to be observed in short periods of time, and the collected data can be stored on magnetic tape for future use, as well as displayed on paper or on oscilloscopes. The digital nature of the data allows mathematical operations such as addition, multiplication, and/or integration to be carried out on the spectra. These allow the data to be processed quickly and more accurately than the spectra obtained from earlier types of instruments where the only record consisted of the analog spectrum on a paper chart. Despite these increases in the speed of data manipulation, the typical methods used to analyze the spectra are essentially those used before the advent of sophisticated digital displays.

Phase One of the Study

A Digilab FTS was used to obtain spectra of ground-level ambient air samples for path lengths ranging from 10 m to 1 km with high spectral resolution (0.1 cm^{-1}) between 500 and

EP 1.89/2:

READEX FICHE best copy available

3500 cm^{-1}. Solar spectra in the same spectral region were also obtained. These spectra were searched for the presence of absorption features of a number of gases. In addition to the well-known lines of gases such as H_2O, CO, CO_2, N_2O, CH_4, and O_3, absorption due to CCl_2F_2 near 1160 cm^{-1} was observed in solar spectra. A mean tropospheric abundance of about 0.34 ppb was estimated. To aid in this search a computer program was written to allow synthetic spectra to be calculated by using the compilation of the line parameters of atmospheric gases prepared by the Air Force Geophysical Laboratories. This program was used to calculate spectra to match the absorption observed in experimental spectra of ground level air samples of path lengths of approximately 10, 100, and 1000 m, and solar spectra corresponding to both high and low sun elevations. These synthetic spectra showed generally good agreement with the observed spectra although some deficiencies in the AFGL line compilation were observed. An atlas of computer-generated infrared transmission spectra of the atmosphere for low and high humidity for a path length of 3 km at 296 K and 1013 mb between 700 and 3000 cm^{-1} was also prepared.

Additional spectra of ground-level air samples and solar spectra were obtained and explorations of the best methods of analyzing these spectra to retrieve accurate estimates of the abundances of atmospheric gases were continued. These methods included spectral ratioing of the air spectra to remove the features of each individual absorbing gas one at a time and by using observer judgment to estimate when the best removal had been obtained. It was found that this method allowed the abundances of gases in ground-level air samples to be estimated with precisions of a few percent. However, the method could not be used to analyze solar spectra because the atmospheric absorbing path is inhomogeneous.

The next method attempted was to remove the absorption features of the individual gases from the air spectrum by ratioing the air spectrum with spectrum calculated from the AFGL line listing. Some success was achieved in analyzing a CO spectrum, although the precision with which the amount of CO in the sample could be estimated was again of the order of a few percent. This technique was used to retrieve the amounts of CO, N_2O, and CO_2 in a 171 m path of ground-level air. These amounts were obtained with estimated precisions of a few percent. Portions of a solar spectrum analyzed in this way allowed the CCl_2F_2 feature near 1160 cm^{-1} to be revealed clearly.

An attempt was made to increase the precision of the abundance estimates by converting the observer signals to absorbances and comparing these latter with the corresponding absorbances of the individual gases as calculated from the line parameters. This method of analyzing a ground-level air spectrum enabled the abundances of N_2O and CO to be estimated with precision of the order of 1%. It was found, however, that the abundance estimates depended on the estimated position of the background signal in the absence of the absorber and on the spectral region analyzed. The position of the background was based on the judgment of the observer. Other differences could be due to the use of incorrect line parameter values to calculate the synthetic spectra.

The ground-level air spectrum was reanalyzed by using a nonlinear, least-squares regression method. In this method the position of the background and the spectral resolution are estimated, in addition to the abundances of the absorbing gases in the sample. It was shown that the abundances estimated in this manner showed a precision somewhat better than that obtained by linear regression analysis of the absorbances and that there was less dependence of the absorber amounts on the spectral region analyzed. This improvement was due primarily to the removal of the observer from the process of determining the background and the spectral resolution of the observed spectrum.

The problems associated with the accurate estimation of the abundances of absorbing atmospheric gases from spectra of air samples have been explored in greater depth.

In these analyses, empirical models or models based on theoretical considerations are used to describe the spectra. The values of the adjustable parameters in these models, their asymptotic standard deviations, and their asymptotic correlation matrices are estimated by curve fitting the experimental spectral data.

Estimates of the "nuisance" parameters, such as the position of the background in the absence of the absorber and the spectral resolution, can be obtained in addition to other information. Some examples of the types of information that can be retrieved include the following:

- The retrieval of the individual absorbing gas amounts in a mixed sample together with its temperature and pressure. This requires a knowledge of the individual line parameters or a suitable collection of reference spectra of the absorbing gases.
- The determination of the mixing ratios of absorbing atmospheric gases by analyzing solar spectra collected at ground level.
- The retrieval of the individual line positions, intensities, and widths from spectra of groups of Voight- or Lorentz-shaped lines.
- The simultaneous analysis of entire rotation-vibration bands to retrieve the upper and lower state molecular constants, the band intensity parameters, and the line-broadening parameters.

The accuracy of the results depends on the correctness of the models used. The precision of the parameter estimates depends on the quality of the spectrum analyzed. In addition to analyzing spectra, the techniques can be used to predict the precision of the parameter estimates for a given experimental design. Thus, quantitative criteria for choosing between different designs can be established.

The methods can be applied to other types of experimental data. However, if the data sets are large and many parameters are to be retrieved, extensive computer time is required.

Phase Two of the Study

The photochemical experiments were carried out using a Digilab FTS-20 (model 496 interferometer) coupled to a photolysis cell. The large, evacuable cell was constructed of 30.5 cm diameter pyrex tubing, 6.3 m long (445 l volume). It housed a modified White optical system which had a base path of 5.3 m and provided a choice of pathlengths which were multiples of eight-times the base length. Most of these experiments were carried out at 170 m (32 traversals) which gave adequate absorption for the compounds studied here in the ppm

concentration range. One cell endplate was equipped with KBr windows to allow the passage of the analytical IR beam. A liquid-helium-cooled Cu:Ge detector was employed in most experiments (450-2400 cm^{-1} range), while a liquid-nitrogen-cooled In:Sb detector was used when an expanded range of spectral response was desired (to $\lambda <$ 4000 cm^{-1}). Potential problems created by varying background absorption from H_2O and CO_2 in the air path between the transfer optics, Nernst glower IR source, interferometer, cell, and detector, were substantially lowered by enclosing the entire optical system in a plastic (acrylic) housing which was purged continuously with nitrogen gas. Open dishes of solid NaOH and KOH were placed in the housing to keep CO_2 levels low.

The large photochemical cell was illuminated by black-light fluorescent lamps which surrounded it. An outer reflective shield of aluminum encompassed both the lamps and the cell. The cell lighting was designed to mimic ground-level solar radiation, both in distribution and intensity, within the photochemically important region 300-450 nm. Room air was circulated in the space between the lamps and the cell to help stabilize the cell temperature. Thermocouples and a thermometer placed inside of the cell were used to determine the actual cell temperature during an experiment. The temperature of the cell could be varied from experiment to experiment within a small range (15-27°C) by regulation of the room temperature.

Peroxynitric Acid Formation

A kinetic study was made of the time dependence of the photolysis of dilute mixtures of Cl_2, H_2, NO_2, and NO in synthetic air. The major products of the reaction, $ClNO_2$, HCl, $HONO_2$, HO_2NO_2, O_3, N_2O_5, H_2O_2 with smaller amounts of HONO, ClNO, and ClONO were identified and followed *in situ* using long-path, infrared FTS. The possible mechanisms for HO_2NO_2 formation and decay in this system were considered. It was concluded that HO_2NO_2 levels are controlled largely by the reactions: $HO_2 + NO_2 (+M) \rightarrow HO_2NO_2 (+M)$; $2HO_2 \rightarrow H_2O_2 + O_2$; $HO_2NO_2 (+ Wall) \rightarrow$ products. From a kinetic treatment of the HO_2NO_2 data for the dark decay, estimates of the equilibrium constant for the system, $HO_2NO_2 \rightleftharpoons HO_2 + NO_2$, were derived in experiments at several temperatures (28.4 - 20.3°C). A kinetic scheme consisting of 65 elementary reactions is proposed to rationalize the rates of the many different products of the irradiated Cl_2, NO_2, NO, H_2, air mixtures. Computer simulations incorporating the present kinetic information on HO_2NO_2 may rise to the ppb level in the sunlight-irradiated, NO_x-RH-polluted troposphere (25°C).

Study of HOCl and Its Absolute Integrated Infrared Band Intensities

The long-path, infrared FTS was employed in the kinetic study of the products of the photolysis of dilute Cl_2, O_3, H_2 mixtures in excess O_2 and N_2 in experiments at 25 ± 3°C and 700 Torr total pressure. The initial rates of formation of the products of the reaction, HCl, HOCl, and H_2O_2, and O_3 loss were studied as a function of the ratio of reactants, $[H_2]/[O_3]$, over the range of 0.10×10^{-3} to 6.8×10^{-3}. The match of these experimental data with computer-generated rate data employing a rather complete reaction set was used to test the mechanism and refine some of the rate constant estimates. From these data, the absolute extinction coefficients for the three fundamental bands of HOCl were derived. The integrated band intensities for the ν_1, ν_2, ν_3 absorption regions were estimated to be 2.3×10^2, 3.0×10^2, and 4.3×10^1 cm^{-2} atm^{-1}, respectively.

Formation of Nitrosamines and Nitramines

The kinetics of the reactions of the $(CH_3)_2N$ radical with NO, NO_2, and O_2 were studied using FTIR spectroscopy. The photolysis of $(CH_3)_2N-N=O$ and $(CH_3)_2N-N=N-N(CH_3)_2$ in dilute mixtures proved to be excellent homogeneous sources of the CH_3N radical. The products of the $(CH_3)_2N$ radical reactions in NO, NO_2, O_2 mixtures were identified as primarily $(CH_3)_2N-N=O$, $(CH_3)_2N-NO_2$, $CH_2=N-CH_3$ with small amounts of $HONO_2$, H_2CO and traces of HCN. In these studies a large reactivity difference for $(CH_3)_2N$ radicals with O_2 and NO or NO_2 was observed; the rate constants for $(CH_3)_2N$ with NO and NO_2 are $(6.8 \pm 0.3) \times 10^{-5}$ and $(2.6 \pm 0.2) \times 10^{-6}$ times that for the reaction of $(CH_3)_2N$ with O_2. This suggests that $(CH_3)_2N-N=O$ and $(CH_3)_2N-NO_2$ may form in the atmosphere at significant rates even when the NO and NO_2 concentrations are in the 10 pphm range. The dimethylnitramine, CH_3N-NO_2, is not photochemically active in the lower atmosphere and would therefore likely be a major product of dimethylamine photooxidation in an NO_x-polluted troposphere.

Recommendations

In the first phase of this work we have developed a new approach to the retrieval of information from infrared spectra of gases and it has been applied to the analysis of many types of spectra. It has been demonstrated that more information, with higher precision can be retrieved than has previously been recognized. The applications of nonlinear, least-squares techniques investigated under this grant have been exploratory in nature, and it has not been possible to explore all the possible uses which have occurred to us. Provided suitable computer programs are available large bodies of data can be analyzed rapidly and accurately and this method should prove useful to many other workers provided descriptions of the programs and their use are made available.

In the second phase of this work we have demonstrated the quantitative nature of the results which may be obtained using long-path, FTS in the study of complex chemical reactions of importance in atmospheric transformations. It is clear that important kinetic and mechanistic information can be obtained for many of the metastable compounds which are expected to be generated in the polluted atmosphere. It is recommended that the Environmental Protection Agency utilize the Fourier transform infrared spectroscopic methods for the unambiguous detection and analysis of metastable complex species which are deemed to be of significance in the control of air pollution.

U.S. GOVERNMENT PRINTING OFFICE: 1981-757-012/7116

This Project Summary was authored by ***John W. Spence*** *who was also the EPA Project Officer (see below).*

The complete report, entitled "Applications of Fourier Transform Spectroscopy to Air Pollution Problems," was authored by John H. Shaw and Jack G. Calvert who are with the Ohio State University Research Foundation, Columbus, OH 43212.

This report (Order No. PB 81-120 792; Cost: $12.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
EPA 335

Official Business
Penalty for Private Use $300